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THE EFFECT OF ALKALI TREATMENT ON COCOAS.

By EUGENE BLOOMBERG, *formerly Assistant Chemist, Buffalo Food and Drug Inspection Station.*

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PURPOSE OF THE INVESTIGATION.

IN THE PROCESS of the manufacture of cocoa, the cocoa beans are roasted, the shells removed, the nibs crushed in a mill, and the resultant product placed in a press whereby a part of the cocoa butter is removed. The press cake is then ground and sifted to form the cocoa of commerce. By the removal of this portion of fat the color of the cocoa is made considerably lighter. For many years it has been the endeavor of manufacturers of cocoa to darken the color of the cocoa so that it would more closely resemble chocolate. This effect has been sought in various ways, but the most prevalent method is by the addition of alkalies or alkaline carbonates. Ammonium carbonate and magnesium carbonate have also been used with this end in view. In this article the term "alkali treatment" will be understood to include the treatment of cocoa not only with the alkalies or alkaline carbonates, but also with such salts as ammonium carbonate and magnesium carbonate. This process is quite generally known as the "Dutching" process, and the cocoas made therefrom as "Dutched" or "Dutch process" cocoas. The name is derived from the fact that this method of treating cocoa originated in Holland.

Attempts have been made at various times to develop this enhanced color by means other than the addition of chemicals. Treatment with steam, under pressure; wetting the cocoa and allowing

it to ferment and then stopping the fermentation by heat; or simply adding water to the cocoa and heating the product to drive off this added water, have all been employed. When alkalies are used, the cocoa beans are partly roasted, then cracked, and the shells removed. The nibs are then treated, either in the roaster or in a separate kettle, with the salt dissolved in water, or, in the case of magnesium carbonate, made into an emulsion with water. The roast is then finished, heat being applied gradually to drive off the water completely. Sometimes this procedure is varied by roasting the beans entirely and cracking and winnowing them, adding the chemical to the cracked nibs in a water-jacketed kettle and applying heat until the product is dry. Although the first occasion for the employment of any of these methods was undoubtedly an attempt to develop a darker color in cocoas, it was later claimed that the alkali treatment renders the cocoa more soluble in water. There is practically no doubt that any of these treatments produces a cocoa which forms a more perfect suspension in the cup and which does not separate as readily from the water solution as does an untreated cocoa. This is largely due to the fact that a portion of the starch is gelatinized by the action of the water in the treatment of the cocoa. It is also claimed that the alkali disintegrates some of the cell walls, and in this way enables the cocoa to stand up better in the cup.

This investigation was undertaken primarily with a view to ascertaining whether the alkali treatment does in fact render the cocoa more soluble, and what changes take place in the cocoa as a result of this treatment. Comparatively little work has been done on the subject of alkali-treated or "Dutched" cocoas, and practically none with the object of the investigation here reported.

Farnsteiner [1] has made an exhaustive study of the effect on the cocoa ash of the addition of varying amounts of potassium carbonate and magnesium carbonate to cocoa. His work was carried out by treating the raw cocoa bean, which had been shelled and ground as finely as possible, with a definite amount of these reagents, ashing the mixture, and determining the ash constants on this product. In addition to this, he has worked out formulas for the determination of the amount of alkali used. He also examined a large number of cocoas in the same way, and endeavored from his researches to determine the percentage and kind of alkali employed. Other references to treated cocoas may be found in "Cocoa and Chocolate." [2] Practically the only subjects treated of in this book are the ash constants and the method of manufacture of Dutch process cocoa.

[1] Z. Nahr. Genussm. (1908) **16:** 625-645.

[2] Whymper. P. Blakiston's Son & Co. (1912): 103-110, 117, 231-238.

DESCRIPTION OF INVESTIGATIONAL SAMPLES.

Practically all samples analyzed in this investigation were obtained directly from the manufacturer, the kind and percentage of alkali employed being known in nearly every case. As far as possible, samples were obtained from the same manufacturer of both treated and untreated cocoas made from the same blend of beans, ascertaining where possible what beans were used in the blend. The samples taken represent the products of a large majority of the manufacturers of so-called "Dutch process" cocoa in this country, and also four of the most popular foreign brands. In addition to these, samples were taken of plain cocoas manufactured by those concerns which made no "Dutch process" cocoa, for the purpose of determining the constants of a plain cocoa which could by no means be contaminated with a "Dutched" cocoa. Moisture and fat determinations were made on each sample so that all other determinations could be calculated to a moisture and fat free basis and the results made comparable. Table 1 gives the number of each sample, the variety of bean, the kind and percentage of alkali, and the amount of moisture and fat. Moisture was determined by drying at the temperature of boiling water for four hours. The fat was determined by extracting the sample in a Knorr extractor with anhydrous ether for four hours.

TABLE 1.—*Description of samples.*

No.	Blend.	Kind and percentage of alkali.	Moisture.	Fat.
			Per cent.	*Per cent.*
1		Untreated	4.07	17.81
2	Same as 1	2.5 per cent potassium carbonate	2.34	18.98
3	Accra, Bahia, Guyaquil	Steam treated	4.31	18.45
4	Accra, Sanchez	3 per cent potassium carbonate	1.98	21.15
5	Guyaquil, Bahia	2.5 per cent potassium carbonate	2.47	23.56
6	do	0.32 per cent ammonium carbonate, 1.65 per cent potassium bicarbonate, 0.15 per cent sodium bicarbonate.	4.40	20.65
7	Sanchez, Guyaquil	2.84 per cent sodium bicarbonate	3.73	20.90
8	Guyaquil, Sanchez, La Guaira, Bahia.	2 per cent potassium bicarbonate, 1 per cent ammonium carbonate.	3.49	20.23
9	Trinidad, La Guaira, Bahia, San Thome.	0.66⅔ per cent potassium carbonate, 0.33⅓ per cent ammonium carbonate.	3.49	18.22
10	Bahia, Arriba, Trinidad, Porto Cabello, Maracaibo, Ceylon.	2 per cent potassium bicarbonate, 1 per cent ammonium carbonate.	3.94	19.20
11		2.5 per cent potassium carbonate	2.92	25.28
12		do	3.03	17.90
13		Untreated	3.78	16.62
14		Water treated	3.07	20.12
15	Same as 11	2.5 per cent potassium carbonate, 10 per cent water.	3.19	25.48
16	Same as 12	1.5 per cent potassium carbonate, 1.5 per cent sodium carbonate.	4.55	20.68
17		Sodium carbonate	2.74	22.37
18		do	2.60	21.18
19	Sanchez, Trinidad	Untreated	3.62	21.28
20	do	2.5 per cent sodium carbonate	2.50	21.25
21		2 per cent sodium carbonate	2.81	23.21
22		1 per cent potassium carbonate	1.95	20.68
23	Same as 22	Untreated	2.65	15.89
24		1 per cent potassium carbonate	1.80	18.84
25		Untreated	4.30	22.71
26	Same as 25	4 per cent ammonium carbonate	4.78	20.18
27		Fermentation process	3.83	28.35
28	Bahia	1 per cent potassium carbonate	4.38	17.42

TABLE 1.—*Description of samples*—Continued.

No.	Blend.	Kind and percentage of alkali.	Moisture.	Fat.
			Per cent.	*Per cent.*
29	Bahia	Untreated	5.00	17.96
30		do	3.30	21.59
31	Same as 30	2 per cent sodium carbonate	3.25	20.63
32		Untreated	4.56	12.37
33	Same as 32	3 per cent sodium bicarbonate	3.50	16.54
34	Imported cocoa, alkali treated		4.64	28.37
35	do		4.60	27.4
[1]36		Untreated	3.75	24.44
37	Imported cocoa, alkali treated		5.13	25.10
38	do		3.96	24.42
[1]39		Untreated	2.81	22.50
[1]40		do	4.80	25.20
[1]41		do	4.18	23.42
[1]42	Arriba, Trinidad	do	2.05	23.52
[1]43	Arriba, Bahia, Accra, Sanchez	do	2.00	23.22
44		do	3.61	15.52
45		do	3.90	26.01
46	Same as 44	1 per cent of a mixture of magnesium carbonate and potassium carbonate.	3.66	18.77
47		Untreated	4.62	18.60
48		do	4.73	21.83
49		1 per cent of a mixture of magnesium carbonate and potassium carbonate.	2.75	28.40
50		1.75 per cent magnesium carbonate	3.00	30.00
51		Untreated	4.78	25.94
52		2 per cent of a mixture of magnesium carbonate and potassium carbonate.	3.70	19.83
53		1.5 per cent of a mixture of magnesium and potassium carbonates.	6.12	28.63
54		Untreated	5.31	21.98
[1]55		do	2.83	21.23
[1]56		do	2.46	24.48
[1]57		do	5.08	22.68
[1]58		do	5.21	22.68

[1] Manufactured by concerns which make no "Dutch process" cocoa.

As the percentage of moisture in the alkali-treated cocoas varies from 1.80 to 6.12 per cent, and in the untreated cocoas from 2 to 5.31 per cent, it is evident that practically all the water which is added in the treatment is driven off.

The percentage of fat in the alkali-treated cocoas varies from 16.54 to 30 per cent; that in the untreated cocoas varies from 12.37 to 26.01 per cent. Judging from these results, it is possible to remove more fat from the untreated cocoa than from a treated one, inasmuch as there are three samples of the untreated cocoas which contain less fat than the minimum of the treated cocoas. In cases where the treated and untreated cocoas are made from the same blend of beans and in the same way, almost invariably the alkali-treated cocoa contains a higher percentage of fat.

ANALYSES OF UNTREATED AND TREATED COCOAS.

Determinations of total ash, water-soluble and water-insoluble ash, alkalinity of the soluble ash, alkalinity of the insoluble ash, and protein were made on each sample. The Gunning method was used for the determination of nitrogen. The other determinations were made in the ordinary way, using methyl orange as an indicator in the titration of the alkalinities. The results obtained are given in Table 2, which contains the analyses of the untreated cocoas, Table 3,

containing the analyses of the treated cocoas, and Table 4, showing the result of alkali treatment by listing the treated and untreated cocoas of the same blend together. All results are calculated to a moisture- and fat-free basis.

TABLE 2.—*Analyses of untreated cocoas.*

No.	Ash.			Alkalinity of ash (N/10 acid per gram of sample).			Protein (Nx6.25).
	Total.	Water-soluble.	Water-insoluble.	Water-soluble.	Water-insoluble.	Total.	
	Per cent.	*Per cent.*	*Per cent.*	*Cc.*	*Cc.*	*Cc.*	*Per cent.*
19	7.94	2.81	5.13	3.05	5.05	8.10	30.32
23	8.57	3.54	5.03	2.70	5.50	8.20	29.84
25	7.54	2.73	4.81	2.40	5.15	7.55	33.31
32	7.16	2.99	4.17	2.55	4.80	7.35	33.48
36	7.05	2.79	4.26	2.25	5.00	7.25	33.20
39	7.50	2.81	4.69	2.30	4.95	7.25	31.33
40	8.30	2.74	5.56	2.35	5.60	7.95	33.43
41	8.16	2.75	5.41	1.95	5.65	7.60	33.84
42	7.28	1.59	5.69	2.50	5.15	7.65	32.03
43	7.17	2.74	4.43	2.25	5.25	7.50	33.63
44	6.94	2.66	4.28	1.90	4.70	6.60	30.02
45	7.63	2.37	5.26	2.35	5.35	7.70	32.74
47	7.32	2.02	5.30	1.80	4.70	6.50	26.78
48	6.99	2.33	4.66	2.10	4.90	7.00	31.58
51	6.94	2.15	4.79	2.00	5.25	7.25	31.61
54	7.80	2.20	5.60	2.00	5.15	7.15	29.79
55	7.95	2.46	5.49	2.45	5.05	7.50	31.68
56	7.56	2.46	5.10	2.45	5.15	7.60	33.54
57	7.56	2.08	5.48	2.20	5.60	7.80	31.49
58	8.97	2.48	6.49	2.35	5.15	7.50	31.55
Maximum	8.97	3.54	6.49	3.05	5.65	8.20	33.84
Minimum	6.94	1.59	4.17	1.80	4.70	6.50	26.78
Average	7.62	2.54	5.08	2.30	5.15	7.45	31.75
1	7.21	3.76	3.45	3.20	4.90	8.10	31.93
13	8.10	4.62	3.48	4.00	4.35	8.35	31.08
29	7.37	3.88	3.49	3.35	4.60	8.00	32.97
30	8.34	4.61	3.73	4.05	5.25	9.30	31.48
3	9.80	7.44	2.36	6.80	4.90	11.70	30.33
14	7.49	4.18	3.31	3.25	4.45	7.70	33.64
27	8.45	1.61	6.84	1.15	6.35	7.50	40.03

Samples 1, 13, 29, and 30 were supposed to have been untreated cocoas, but they were made in a factory which also makes treated cocoas. Judging from the analytical data, they were contaminated with a certain amount of alkali-treated cocoa during the process of manufacture, for which reason they are excluded from the averages. Sample 3 was supposed to have been made by the straight steam treatment in place of having any added alkali. Sample 14 was made by thoroughly soaking the nibs and reroasting. These samples, however, were made only on an experimental scale. Inasmuch as they were run through the regular cocoa machinery in which "Dutch process" cocoa had been made, they were undoubtedly contaminated, as were the other samples. Sample 27 was made by a fermentation process, wetting the nibs and allowing them to ferment for some time in a warm place before finishing the roast. It will be noticed that the indicated protein in this sample is exceptionally high. This would lead to the conclusion that a certain amount

of some ammonium salt was added to these nibs, either during the fermentation or in the water in which they were soaked.

TABLE 3.—*Analyses of alkali-treated cocoas.*

No.	Alkali.	Ash.			Alkalinity of ash (N/10 acid per gram of sample).			Protein (N x 6.25).
		Total.	Water-soluble.	Water-insoluble.	Water-soluble.	Water-insoluble.	Total.	
		Per ct.	*Per ct.*	*Per ct.*	*Cc.*	*Cc.*	*Cc.*	*Per ct.*
4	3 per cent potassium carbonate	11.45	6.52	4.93	7.90	4.20	12.10	32.72
2	2.5 per cent potassium carbonate	8.36	4.89	3.47	4.00	4.90	8.90	31.72
5	do	10.52	6.63	3.90	5.90	4.55	10.45	32.57
11	do	11.49	8.75	2.74	7.25	6.15	13.40	33.18
12	do	11.00	8.08	2.92	7.35	5.40	12.75	33.79
15	2.5 per cent potassium carbonate and 10 per cent water	11.07	8.87	2.20	7.75	4.80	12.55	32.20
28	1 per cent potassium carbonate	8.31	5.98	2.33	5.10	4.80	9.90	33.04
24	do	9.07	5.22	3.85	4.80	5.35	10.15	31.45
22	do	9.20	5.82	3.38	5.45	5.35	10.80	32.59
33	3 per cent sodium bicarbonate	8.76	6.54	2.22	6.65	5.05	11.70	32.87
7	2.84 per cent sodium bicarbonate	10.48	7.96	2.52	6.60	5.90	12.50	31.09
20	2.5 per cent sodium carbonate	11.45	8.17	3.28	11.15	5.25	16.40	29.57
21	2 per cent sodium carbonate	10.97	8.15	2.82	9.95	4.90	14.85	28.71
31	do	10.23	7.54	2.69	8.60	5.30	13.90	29.62
18	Sodium carbonate	11.39	6.99	4.40	7.70	5.30	13.00	30.45
17	do	9.60	7.32	2.28	8.20	5.15	13.35	32.17
26	4 per cent ammonium carbonate	7.66	2.87	4.79	2.25	5.10	7.35	36.18
50	1.75 per cent magnesium carbonate	8.91	2.43	6.48	2.40	6.20	8.60	30.69
8	2 per cent potassium bicarbonate and 1 per cent ammonium carbonate	9.50	6.97	2.53	6.25	5.40	11.65	31.29
10	do	8.59	5.75	2.84	4.25	5.50	9.75	31.63
16	1.5 per cent potassium carbonate and 1.5 per cent sodium carbonate	11.62	9.36	2.26	10.35	4.85	15.20	31.92
9	0.66 per cent potassium carbonate and 0.33 per cent ammonium carbonate	9.15	5.22	3.83	4.40	5.55	9.95	31.29
52	2 per cent (magnesium carbonate and potassium carbonate)	7.78	4.25	3.53	4.10	5.25	9.35	27.75
53	1.5 per cent (magnesium carbonate and potassium carbonate)	8.29	4.75	3.54	4.45	6.35	10.80	33.52
46	1 per cent (magnesium carbonate and potassium carbonate)	7.87	3.52	4.35	3.15	5.05	8.20	31.31
49	do	9.32	5.08	4.24	4.50	5.00	9.50	30.82
6	1.65 per cent potassium carbonate, 0.15 per cent sodium carbonate, and 0.32 per cent ammonium carbonate	10.69	7.79	2.90	6.90	4.20	11.10	30.97
	Maximum	11.62	9.36	6.48	11.15	6.35	16.40	36.18
	Minimum	7.66	2.43	2.20	2.25	4.20	7.35	27.75
	Average	9.73	6.35	3.38	5.46	5.21	10.67	31.88
34	Imported	10.10	7.94	2.16	7.40	5.35	12.75	33.00
35	do	13.30	9.95	3.35	7.50	3.25	12.75	33.82
37	do	11.42	8.27	3.15	7.10	3.50	10.60	31.35
38	do	11.94	9.80	2.14	9.00	3.00	12.00	30.84

Sample 2 was supposed to have been made by the addition of 2.5 per cent potassium carbonate. The results obtained, however, would seem to indicate the addition of a much smaller quantity than this, probably not more than 1 per cent. Samples 34, 35, 37, and 38 are imported samples, all of which have been treated with alkalis, the kinds and percentages of which are, however, unknown.

The total ash on the samples varies from 7.66 to 11.62 per cent, with an average of 9.73 per cent. The minimum ash is that of a cocoa treated with 4 per cent ammonium carbonate, which will, of course, volatilize in the heating which the product subsequently undergoes. With this exception the lowest ash is 7.78 per cent, being the

ash of a cocoa treated with 2 per cent of a mixture of magnesium and potassium carbonates. The maximum ash, 11.62 per cent, is that of a cocoa treated with 1.5 per cent potassium carbonate and 1.5 per cent sodium carbonate. As would be expected, the ash varies approximately with the amount of alkali added.

Water-soluble ash varies from 2.43 to 9.36 per cent, with an average of 6.35 per cent. The lowest soluble ash is that of a cocoa which is treated with magnesium carbonate, which, of course, is insoluble in water. Next to this is one with a soluble ash of 2.87 per cent, which has been treated with ammonium carbonate. There are several varying from 3.52 to 4.75 per cent, which have been treated with a mixture of magnesium and potassium carbonates. The lowest water-soluble ash of those which are treated with soluble nonvolatile alkalies is 4.89 per cent.

The water-insoluble ash varies from 2.20 to 6.48 per cent, with an average of 3.38 per cent. The lowest insoluble ash was obtained from a cocoa treated with 2.5 per cent potassium carbonate and 10 per cent water. The highest is that of a cocoa treated with 1.75 per cent magnesium carbonate, which is insoluble in water. Aside from this one, the maximum water-insoluble ash is 4.93 per cent.

The alkalinity of water-soluble ash varies from 2.25 to 11.15 cc of N/10 acid per gram. Naturally, those treated with ammonium and magnesium carbonates show the lowest soluble alkalinity. Excluding these, the minimum is 4 cc. As might be expected, the maximum alkalinity is shown in those cocoas which have been treated with sodium carbonate. The alkalinity of the insoluble ash shows no points for discussion. The total alkalinity follows about the same order as the soluble alkalinity and for approximately the same reasons.

The protein varies from 27.75 to 36.18 per cent. This latter figure is attained on sample 26, which was treated with 4 per cent ammonium carbonate. This would probably explain the high protein percentage on the theory that a portion of the ammonia was not volatilized. Excluding this sample, the maximum is 33.79 per cent.

Table 4 shows the effect on the ash constants of the cocoa of the addition of alkali, or the effects of various alkalies on the same blend. Each pair was made from the same blend of beans and treated as stated in Table 4.

The results obtained are those which are normally expected on a treated cocoa, namely, that the total water-soluble ash and the alkalinity of the water-soluble ash are greatly increased, while the water-insoluble ash is decreased. This proves to be the case in every sample except sample 26, which shows practically no change in the ash constants. It is quite evident that the treatment with ammonia has made no change in the ash of the cocoa. Further

tables, however, will show that treatment with ammonia can be recognized by other changes in the analytical data. Sample 46 gives higher figures in all ashes and in all alkalinities than sample 44, due to the fact that it has been treated with both magnesium carbonate and potassium carbonate, the potassium carbonate increasing the water-soluble ash and the water-soluble alkalinity, and the magnesium carbonate increasing the water-insoluble ash and the water-insoluble alkalinity.

TABLE 4.—*Comparison of treated and untreated cocoas.*

No.	Alkali.	Ash.			Alkalinity of ash (N/10 acid per gram of sample).			Protein (N x 6.25).
		Total.	Water-soluble.	Water-insoluble.	Water-soluble.	Water-insoluble.	Total.	
		Per ct.	*Per ct.*	*Per ct.*	*Cc.*	*Cc.*	*Cc.*	*Per ct.*
2	2.5 per cent potassium carbonate	8.36	4.89	3.47	4.00	4.90	8.90	31.72
1	Untreated	7.21	3.76	3.45	3.20	4.90	8.10	31.93
15	2.5 per cent potassium carbonate, 10 per cent water	11.07	8.87	2.20	7.75	4.80	12.55	32.20
11	Without water	11.49	8.75	2.74	7.25	6.15	13.40	33.18
16	1.5 per cent potassium carbonate, 1.5 per cent sodium carbonate	11.62	9.36	2.26	10.35	4.85	15.20	31.92
12	2.5 per cent potassium carbonate	11.00	8.08	2.92	7.35	5.40	12.75	33.79
22	1 per cent potassium carbonate	9.20	5.82	3.38	5.45	5.35	10.80	32.59
23	Untreated	8.57	3.54	5.03	2.72	5.50	8.20	29.84
20	2.5 per cent sodium carbonate	11.45	8.17	3.28	11.15	5.25	16.40	29.57
19	Untreated	7.94	2.81	5.13	3.05	5.05	8.10	30.32
26	4 per cent ammonium carbonate	7.66	2.87	4.79	2.25	5.10	7.35	36.18
25	Untreated	7.54	2.73	4.81	2.40	5.15	7.55	33.31
28	1 per cent potassium carbonate	8.31	5.98	2.33	5.10	4.80	9.90	33.04
29	Untreated	7.37	3.88	3.49	3.35	4.60	8.00	32.97
31	2 per cent sodium carbonate	10.23	7.54	2.69	8.60	5.30	13.90	29.62
30	Untreated	8.34	4.61	3.73	4.05	5.25	9.30	31.48
33	3 per cent sodium bicarbonate	8.76	6.54	2.22	6.65	5.05	11.70	32.87
32	Untreated	7.16	2.99	4.17	2.55	4.80	7.35	33.48
46	1 per cent (magnesium carbonate and potassium carbonate)	7.87	3.52	4.35	3.15	5.05	8.20	31.31
44	Untreated	6.94	2.66	4.28	1.90	4.70	6.60	30.02

Comparison of Tables 2 and 3 shows that the maximum percentage of total ash in the alkali-treated cocoas is 2.65 above that in the untreated cocoas, and the average is 2.11 higher. A wider variation is shown in the water-soluble ash, where the maximum percentage in the alkali-treated is 5.82 higher than the maximum of the untreated cocoas, and the average is 3.81 higher. With the exception of one sample of the treated cocoa, which has had added to it 1.75 per cent magnesium carbonate, the maximum percentage of water-insoluble ash in the untreated cocoa is 1.56 higher than in the treated cocoa, and the average is 1.27 higher. The soluble

alkalinity shows a maximum for the treated cocoas of 8.10 cc above the maximum for the untreated cocoas, and an average of 3.16 cc higher. There is very little difference in the figures on the insoluble alkalinities, and this difference would be still slighter if it were not for those few samples which have been treated with magnesium carbonate and which show a higher water-insoluble alkalinity on that account.

WATER-SOLUBLE MATTER IN UNTREATED AND TREATED COCOAS.

In order to determine the effect of alkali treatment on the solubility of the cocoa, the total water-soluble matter was determined in both treated and untreated cocoas. This was done by rubbing up 10 grams of the cocoa with 250 cc of water, heating to boiling and boiling for a minute, then allowing to stand over night and filtering. Fifty cc of this filtrate, corresponding to 2 grams of the original cocoa, were evaporated to dryness and dried to constant weight. These solids were then ashed, and the total ash, water-soluble ash, water-insoluble ash, alkalinity of the soluble ash, and alkalinity of the insoluble ash determined on each sample. Nitrogen was determined on a 50 cc portion of the filtrate, and protein calculated from this determination. It was noted that on addition of acid to the water solution of the "Dutched" cocoas a flocculent precipitate was thrown down. Upon investigation this proved to be a nitrogenous substance. To determine the amount of this nitrogenous substance present, a measured portion of the water solution of the cocoa was made acid with 1 per cent of sulphuric acid. This was then filtered, and nitrogen was determined upon an aliquot of the filtrate, and the protein calculated therefrom. The difference between the protein as here determined and that of the total water-soluble protein was the nitrogenous substances precipitated by the sulphuric acid. The color value on a brewer's scale of the water solution was determined in a Lovibond tintometer, using a $\frac{1}{4}$-inch cell. In making the water solution the cocoa was weighed as it came, but the results were all calculated to a moisture- and fat-free basis. These results are listed in Tables 5, 6, and 7. Table 5 gives the results obtained on untreated cocoas, Table 6 those on cocoas treated with alkalies, and Table 7 the comparison of the same blend of beans treated in various ways.

The water-soluble matter in the untreated cocoas varies from 29.16 to 35.55 per cent, with an average of 31.58 per cent. In the alkali-treated cocoas it varies from 24.90 to 37.02 per cent, with an average of 32.16 per cent. The minimum was obtained on a sample which was treated with magnesium carbonate, the next lowest being 28.17 per cent. The maximum percentage of water-soluble material in the alkali-treated cocoas is higher than that in the untreated cocoas by 1.47, while the average is 0.58 higher. This increase in solu-

bility is largely accounted for, however, by the water-soluble alkalies which have been added to the treated cocoas. This fact is shown by the percentage of water-soluble material less the ash of the water-soluble material, in which determination the untreated cocoas vary from 23.54 to 30.11 per cent, with an average of 25.53 per cent, while the treated cocoas vary from 19.58 to 28.93 per cent, with an average of 24.66 per cent, the untreated cocoas having a maximum percentage 1.18 higher than the maximum of the treated cocoas, a minimum percentage 3.96, and an average percentage 0.87 higher. There are eight samples of the alkali-treated cocoas which are less than the minimum of the untreated cocoas.

TABLE 5.—*Water-soluble matter in untreated cocoas.*

No.	Water-soluble matter.			Ash of water-soluble matter.						Water-soluble protein (N x 6.25).		Color value 4 per cent solution (½-inch cell, brewer's scale).
	Total.	Ash-free.	Ash- and protein-free.	Total.	Water-soluble.	Water-insoluble.	Alkalinity (N/10 acid per gram of cocoa.)			Total.	Insoluble in 1 per cent sulphuric acid.	
							Water-soluble.	Water-insoluble.	Total.			
	P. ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Cc.*	*Cc.*	*Cc.*	*Per ct.*	*Per ct.*	*Degrees.*
19	33.14	26.79	14.43	6.35	3.54	2.81	2.95	4.65	7.60	12.25	0.00	30.6
23	32.33	24.77	15.26	7.56	3.89	3.67	2.80	4.70	7.50	9.51	0.00	39.3
25	32.55	26.18	15.16	6.37	3.55	2.82	2.35	4.45	6.80	11.03	0.00	31.5
32	32.68	26.93	16.60	5.75	4.02	1.73	3.50	3.35	6.85	10.33	0.00	31.3
36	30.98	24.89	12.37	6.09	3.16	2.93	1.60	4.95	6.55	12.55	0.00	39.0
39	31.89	25.77	13.64	6.12	3.01	3.11	2.00	4.55	6.55	12.13	0.00	32.1
40	31.43	25.66	14.40	5.75	2.06	3.71	2.45	5.05	7.50	11.26	0.00	20.0
41	29.79	23.70	13.67	6.09	2.94	3.15	2.50	4.80	7.30	10.03	0.00	22.1
42	30.15	25.19	14.25	6.96	3.53	3.43	2.50	4.70	7.20	10.94	0.00	21.5
43	29.62	23.54	12.90	6.08	2.83	3.25	2.35	4.75	7.10	10.64	0.00	29.2
44	30.54	24.12	14.11	6.42	3.55	2.87	2.30	4.50	6.80	10.01	0.00	27.2
45	31.25	24.77	13.16	6.48	3.27	3.21	2.50	5.15	7.65	11.61	0.00	20.0
47	29.16	23.68	12.74	5.48	2.87	2.61	2.45	4.15	6.60	10.94	0.00	23.4
48	31.02	25.20	14.29	5.82	2.59	3.24	2.40	4.75	7.15	10.91	0.00	27.2
51	30.04	24.55	13.05	5.49	2.23	3.26	2.15	4.70	6.85	11.50	0.00	31.8
54	32.17	26.54	14.23	5.63	3.04	2.59	2.60	3.95	6.55	12.31	0.00	23.4
55	35.55	30.11	18.94	5.44	3.78	1.66	2.75	3.85	6.60	10.17	0.00	23.7
56	33.07	27.49	17.43	5.58	3.28	2.30	3.10	4.10	7.20	10.06	0.00	24.6
57	33.60	27.77	16.63	5.83	3.81	2.02	2.75	3.70	6.45	11.14	0.00	23.5
58	33.16	25.64	13.63	6.52	3.55	2.97	2.75	4.65	7.40	12.01	0.00	27.7
Max.	35.55	30.11	18.94	7.56	4.02	3.71	3.50	5.15	7.65	12.55	0.00	39.3
Min.	29.16	23.54	12.37	5.44	2.06	1.66	1.60	3.35	6.45	9.51	0.00	20.0
Aver.	31.58	25.53	14.47	6.06	3.22	2.84	2.54	4.35	6.89	11.06	0.00	27.4
1	28.29	21.17	10.78	7.12	4.59	2.53	2.00	3.85	5.85	10.39	0.81	36.8
13	33.69	25.56	14.00	8.13	6.31	1.82	4.90	2.95	7.85	11.56	1.66	34.4
29	31.84	26.15	13.43	5.69	3.91	1.78	3.50	3.75	7.25	12.72	1.96	50.6
30	33.90	26.96	14.79	6.94	4.79	2.15	5.15	3.30	8.45	12.17	.....	29.2
3	28.26	20.88	8.70	7.38	6.08	1.30	5.80	2.40	8.20	12.18	5.03	63.4
14	32.55	25.13	13.15	7.42	5.25	2.17	4.05	3.30	7.35	11.98	1.40	28.6
27	23.21	18.20	9.94	5.01	3.83	1.18	2.50	2.05	4.55	8.26	.....	8.8

TABLE 6.—*Water-soluble matter in alkali-treated cocoas.*

No.	Water-soluble matter.			Ash of water-soluble matter.						Water-soluble protein (N x 6.25).		Color value 4 per cent solution (¼-inch cell, brewer's scale).
	Total.	Ash-free.	Ash- and protein-free.	Total.	Water-soluble.	Water-insoluble.	Alkalinity (N/10 acid per gram of cocoa).			Total.	Insoluble in 1 per cent sulphuric acid.	
							Water-soluble.	Water-insoluble.	Total.			
	P. ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Cc.*	*Cc.*	*Cc.*	*Per ct.*	*Per ct.*	*Degrees.*
4	28.17	19.58	6.66	8.59	7.17	1.42	6.00	2.50	8.50	12.92	5.12	67.4
2	29.59	22.61	10.36	6.98	4.79	2.19	4.45	3.40	7.85	12.25	3.25	53.4
5	29.12	21.05	10.15	8.07	6.07	2.00	6.50	3.20	9.70	10.90	3.50	48.6
11	31.10	22.17	10.83	8.93	7.88	1.05	6.90	2.40	9.30	11.34	2.30	59.9
12	31.27	23.67	12.31	8.60	7.63	.97	6.75	2.90	9.65	11.36	2.67	49.3
15	37.02	27.22	15.53	9.80	9.00	.80	8.00	2.10	10.10	11.29	.79	70.0
28	33.50	25.89	12.86	7.61	6.53	1.08	5.00	3.05	8.05	13.03	2.32	81.8
24	32.74	24.86	14.60	7.88	6.02	1.86	4.70	3.85	8.55	10.26	.38	61.7
22	32.65	24.06	13.80	8.59	6.83	1.76	5.35	3.75	9.10	10.26	.94	67.3
33	31.26	24.76	13.76	6.50	5.12	1.38	6.80	2.00	8.80	11.00	1.21	81.4
7	31.40	22.84	12.39	8.56	7.43	1.13	6.95	2.70	9.65	10.45	1.65	59.7
20	36.72	28.93	17.27	7.79	7.17	.62	10.25	2.10	12.35	11.66	3.15	98.4
21	33.72	24.62	13.62	9.10	8.38	.72	8.70	2.90	11.60	11.00	.73	85.2
31	34.35	26.80	14.39	7.55	6.37	1.18	10.30	2.25	12.55	12.41	3.55	76.2
18	34.48	27.11	15.73	7.37	6.53	.84	9.05	2.52	11.55	11.38	1.72	85.3
17	35.93	27.76	15.53	8.17	6.77	1.40	8.80	2.55	11.35	12.23	2.79	86.8
26	33.42	28.22	15.16	5.20	4.10	1.10	2.50	3.15	5.65	13.06	1.77	68.0
50	24.90	20.15	10.49	4.75	3.25	1.50	3.65	4.40	8.05	9.66	1.05	49.2
8	32.09	24.46	13.38	7.63	6.69	.94	5.85	3.15	9.00	11.08	1.63	47.2
10	34.38	26.57	14.13	7.81	6.51	1.30	4.25	3.70	7.95	12.44	1.48	29.3
16	36.00	25.26	12.26	10.74	8.77	1.97	10.45	2.40	12.85	13.00	3.54	93.6
9	33.94	26.60	14.59	7.34	5.83	1.51	5.10	3.65	8.75	12.01	1.37	25.5
52	30.54	26.05	14.61	4.49	3.56	.93	4.60	2.85	7.45	11.44	1.83	75.8
53	33.15	28.26	15.98	4.89	3.94	.95	5.00	2.60	7.60	12.28	1.22	69.0
46	28.82	23.80	12.30	5.02	3.79	1.23	3.95	3.45	7.40	11.50	2.19	45.4
49	29.68	23.10	13.95	6.58	5.05	1.53	4.50	3.45	8.05	9.15	.89	36.3
6	28.34	20.31	9.16	8.03	6.67	1.36	6.50	2.20	8.70	11.15	4.55	73.4
Max.	37.02	28.93	17.27	10.74	9.00	2.19	10.45	4.40	12.85	13.06	5.12	98.4
Min.	24.90	19.58	6.66	4.49	3.25	.62	2.50	2.00	5.65	9.15	.38	25.5
Avg.	32.16	24.66	13.16	7.50	6.22	1.38	6.33	2.93	9.26	11.50	2.13	64.7
34	39.22	32.38	18.86	6.84	6.42	.42	7.55	1.35	8.90	13.52	3.45	111.9
35	33.57	24.55	13.92	9.02	7.89	1.13	7.75	2.10	9.85	10.63	2.19	107.5
37	42.01	33.68	17.81	8.33	7.58	.75	7.15	2.45	9.60	15.87	4.83	114.7
38	38.79	30.93	15.78	7.86	7.43	.43	8.40	1.85	10.25	15.15	3.35	101.9

These figures show that treatment with alkali does not increase the solubility of the cocoa material, but rather diminishes this solubility. Inasmuch as it was to be expected that treatment with alkali would increase the solubility of the protein and this expectation is borne out by the results obtained, the decrease in solubility must be due to the fact that the presence of the alkali has an inhibitory action on the solution of some of the nonnitrogenous substances. This is plainly shown in the third column of Tables 5 and 6, where the total solids less the protein and ash are calculated. Here the untreated cocoas range from 12.37 to 18.94 per cent, with an average of 14.47 per cent, while the treated cocoas range from 6.66 to 17.27 per cent, with an average of 13.16 per cent, the maximum percentage for untreated cocoa being 1.67 higher than that for the treated cocoa, the minimum 5.71 higher, and the average 1.31 higher. Nine samples of alkali-treated cocoa have less than the minimum of the untreated cocoa.

As might be expected, the ash of the soluble matter varies about the same as the ash of the cocoa.

The water-soluble protein is slightly higher in the alkali-treated cocoas than in the untreated cocoas, the maximum percentage being 0.51 higher, and the average 0.44 higher. The percentage of water-soluble protein insoluble in 1 per cent sulphuric acid, however, seems to be an important determination. In every case where the cocoa had been treated, more or less nitrogenous matter was precipitated by the addition of 1 per cent of sulphuric acid to the water-solution of the cocoa. This nitrogenous matter, calculated as protein, ranged from 0.38 to 5.12 per cent. The total water-soluble protein was not increased by any such figure. This would tend to show either that the alkali treatment inhibited the solution of some of the nitrogenous substances which would normally be dissolved by the water, or that some substance was dissolved by the alkali, which on the addition of sulphuric acid had precipitated some of the protein which was normally water-soluble. The untreated cocoas showed no precipitate on the addition of 1 per cent of sulphuric acid, the only exceptions to this being samples 1, 13, and 29, which have already been set aside on the ground that they were more or less contaminated with alkali-treated cocoas, having been made in a factory which also makes alkali-treated cocoas and passed through the same machinery. In no case where the sample was made by a firm which makes no alkali-treated cocoa was there any precipitate.

As might have been expected, the alkali treatment greatly enhanced the color of the water solution. The color values of the untreated cocoas ranged from 20 to 39.3, with an average of 27.4, those of the treated cocoas from 25.5 to 98.4, with an average of 64.7. Only three of the alkali-treated cocoas showed a color value of less than 46.4, and 16 showed a color value of over 60. The maximum of the alkali-treated cocoas was 59.1 above the maximum for the untreated cocoas, and the average was 37.3 above the average for the untreated cocoas.

Samples 1 and 2, representing the same blend of cocoas, sample 1 being untreated and sample 2 treated with 2.5 per cent potassium carbonate, show the effect of treatment. The total water-soluble matter, the water-soluble matter less the ash, the water-soluble protein, and the color value are increased by the alkali treatment. The nonnitrogenous, nonash soluble solids, however, are found in large amount in the untreated cocoa. Samples 15 and 11 represent the same blend of beans and the same alkali, but, in addition to the alkali, sample 15 had added to it 10 per cent of water in the treatment. This water treatment largely increased the soluble matter and deepened the color. Sample 16 was made with 1.5 per cent potassium carbonate and 1.5 per cent sodium carbonate, while sample 12 was made with 2.5 per cent potassium carbonate. The mixed carbonates in-

creased the total water-soluble matter and the water-soluble matter minus the ash, but the nonnitrogenous, nonash soluble matter did not vary. Of course, the increase in total amount of alkali increased the ash constants throughout. The greatest difference shown by these two treatments is the large increase in the color value of the solution by the use of the mixed carbonates. As will be shown later, this large increase in color is due principally to the action of the sodium carbonate.

TABLE 7.—*Comparison of water-soluble matter in treated and untreated cocoas.*

No.	Water-soluble matter.			Ash of water-soluble matter.						Water-soluble protein (N x 6.25).		Color value 4 per cent solution (¼-inch cell, brewer's scale).
							Alkalinity (N/10 acid per gram of cocoa).					
	Total.	Ash-free.	Ash- and protein-free.	Total.	Water-soluble.	Water-insoluble.	Water-soluble.	Water-insoluble.	Total.	Total.	Insoluble in 1 per cent sulphuric acid.	
	P. ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Cc.*	*Cc.*	*Cc.*	*Per ct.*	*Per ct.*	*Degrees.*
2	29.59	22.61	10.36	6.98	4.79	2.19	4.45	3.40	7.85	12.25	3.25	53.4
1	28.29	21.17	10.78	7.12	4.59	2.53	2.00	3.85	5.85	10.39	.81	36.8
15	37.02	27.22	15.53	9.80	9.00	.80	8.00	2.10	10.10	11.29	.79	70.0
11	31.10	22.17	10.83	8.93	7.88	1.05	6.90	2.40	9.30	11.34	2.30	59.9
16	36.00	25.26	12.26	10.74	8.77	1.97	10.45	2.40	12.85	13.00	3.54	93.6
12	31.27	23.67	12.31	8.60	7.63	97	6.75	2.90	9.65	11.36	2.67	43.3
22	32.65	24.06	13.80	8.59	6.83	1.76	5.35	3.75	9.10	10.26	.94	67.3
23	32.33	24.77	15.26	7.56	3.89	3.67	2.80	4.70	7.50	9.51	.00	39.3
20	36.72	28.93	17.27	7.79	7.14	.62	10.25	2.10	12.35	11.66	3.15	98.4
19	33.14	26.79	14.43	6.35	3.54	2.81	2.95	4.65	7.60	12.25	.00	30.6
26	33.42	28.22	15.16	5.20	4.10	1.10	2.50	3.15	5.65	13.06	1.77	68.0
25	32.55	26.18	15.16	6.37	3.55	2.82	2.35	4.45	6.80	11.03	.00	31.5
28	33.50	25.89	12.86	7.61	6.53	1.08	5.00	3.04	8.05	13.03	2.32	81.8
29	31.84	26.15	13.43	5.69	3.91	1.78	3.50	3.75	7.25	12.72	1.96	50.6
31	34.35	26.80	14.39	7.55	6.37	1.18	10.30	2.25	12.55	12.41	3.55	76.2
30	33.90	26.96	14.79	6.94	4.79	2.15	5.15	3.30	8.45	12.17	.00	29.2
33	31.26	24.76	13.76	6.50	5.12	1.38	6.80	2.00	8.80	11.00	1.21	81.4
32	32.68	26.93	16.60	5.75	4.02	1.73	3.50	3.35	6.85	10.33	.00	31.3
46	28.82	23.80	12.30	5.02	3.79	1.23	3.95	3.45	7.40	11.50	2.19	46.4
44	30.54	24.12	14.11	6.42	3.55	2.87	2.30	4.50	6.80	10.01	.00	27.2

Sample 22 was treated with 1 per cent potassium carbonate and shows a slightly increased total soluble matter, but less ash-free soluble matter and protein- and ash-free soluble matter. The alkali treatment shows an increase in the color value and the expected increase in the ash constants. Sample 20, treated with 2.5 per cent sodium carbonate, shows an increase in the soluble solids throughout and in the color value. Sample 26, treated with 4 per cent ammonium carbonate, shows a slight increase in the amount of soluble matter and in the color value of the solution. Sample 28, treated with 1 per cent sodium carbonate, shows a larger percentage of total soluble solids, but a smaller percentage of ash-free and protein- and ash-free

soluble matter. The color value has also been increased. Sample 29, however, shows from the analysis that a certain percentage of alkali-treated cocoa is present with it, so that the variations are not as great as might be expected. Sample 31, treated with 2 per cent sodium carbonate, shows a comparatively small variation in the soluble matter, but a large difference in the color value. Sample 33, treated with 3 per cent sodium bicarbonate, shows a diminution of the soluble matter, but an increased color value. Sample 46, which has been treated with 1 per cent of a mixture of magnesium and potassium carbonates, shows less soluble matter than a like sample untreated, but shows some increase in the color value of the solution.

COMPOSITION OF THE WATER-SOLUBLE MATTER IN UNTREATED AND TREATED COCOAS.

Tables 5, 6, and 7 give the analyses of the water-soluble matter as calculated back to the original cocoa. It was deemed advisable to calculate the composition of the water-soluble solids of the cocoa. This calculation is given in Tables 8 and 9. Comparison of these tables shows that the alkali treatment makes a marked difference in the composition of the water-soluble matter. Naturally the water-soluble matter from the alkali-treated cocoas contains a higher percentage of ash (4.05 on the average), a higher percentage of soluble ash (9.10 on the average), and less insoluble ash (5.05 on the average). The alkalinities of the ash are also higher on the treated cocoas, and the percentage of the total calculated protein is higher by 1.04 on the average.

TABLE 8.—*Composition of the water-soluble matter of untreated cocoas.*

No.	Ash.			Alkalinity of ash (N/10 acid per gram of sample).			Protein.		Ash-free and protein-free solids.
	Total.	Water-soluble.	Water-insoluble.	Water-soluble.	Water-insoluble.	Total.	Total.	Precipitated by 1 per cent sulphuric acid.	
	P. cent.	*P. cent.*	*P. cent.*	*Cc.*	*Cc.*	*Cc.*	*P. cent.*	*P. cent.*	*P. cent.*
19	19.16	10.68	8.48	8.85	14.05	22.90	36.96	0.00	43.88
23	23.39	12.03	11.36	8.75	14.40	23.15	29.42	0.00	47.19
25	19.57	10.90	8.67	7.15	13.70	20.85	33.88	0.00	46.55
32	17.60	12.30	5.30	10.70	10.30	21.00	31.60	0.00	50.80
36	19.64	10.20	9.44	5.15	14.40	19.55	40.49	0.00	39.87
39	19.18	9.45	9.74	6.30	14.30	20.60	38.03	0.00	42.79
40	18.20	6.49	11.71	7.65	16.00	23.65	35.50	0.00	46.30
41	20.45	9.88	10.57	8.35	16.20	24.55	33.66	0.00	45.89
42	23.09	11.72	11.37	8.25	15.60	23.85	36.29	0.00	40.52
43	20.73	9.66	11.07	7.95	16.15	24.10	36.26	0.00	43.01
44	21.01	11.62	9.39	7.50	14.80	22.30	32.79	0.00	46.20
45	20.73	10.46	10.27	8.00	16.45	24.45	37.17	0.00	42.10
47	18.80	9.83	8.97	8.50	14.05	22.55	37.52	0.00	43.68
48	18.79	8.34	10.45	7.70	15.35	23.05	35.16	0.00	46.05
51	18.29	7.41	10.88	7.20	15.65	22.85	38.80	0.00	42.91
54	17.49	9.45	8.04	8.10	12.20	20.30	37.97	0.00	44.54
55	15.30	10.63	4.67	7.80	10.75	18.55	26.74	0.00	57.96
56	16.89	9.94	6.95	9.30	12.40	21.70	30.42	0.00	52.79

TABLE 8.—*Composition of the water-soluble matter of untreated cocoas*—Continued.

No.	Ash.			Alkalinity of ash (N/10 acid per gram of sample).			Protein.		Ash-free and protein-free solids.
	Total.	Water-soluble.	Water-insoluble.	Water-soluble.	Water-insoluble.	Total.	Total.	Precipitated by 1 per cent sulphuric acid.	
	P. cent.	*P. cent.*	*P. cent.*	*P. cent.*	*P. cent.*	*P. cent.*	*P. cent.*	*P. cent.*	*P cent.*
57	17.35	11.35	6.02	9.25	10.90	19.15	33.16	0.00	49.49
58	19.66	10.71	8.95	8.35	14.00	22.35	36.22	0.00	44.12
Maximum	23.39	12.30	11.71	10.70	16.45	24.55	40.49	0.00	57.96
Minimum	15.30	6.49	4.67	5.15	10.30	18.55	26.74	0.00	39.87
Average	19.27	10.16	9.11	8.01	14.08	22.09	34.91	0.00	45.83
1	25.16	16.22	8.94	7.10	13.60	20.70	36.72	2.86	38.12
13	24.13	18.73	5.40	14.55	8.75	23.30	34.31	4.92	41.56
29	17.86	12.27	5.59	11.00	11.80	22.80	39.95	6.15	42.19
30	20.46	14.14	6.32	15.10	9.80	24.90	35.90	0.00	43.60
3	26.11	21.51	4.60	20.50	8.50	29.00	43.10	17.80	30.79
14	22.80	16.20	6.60	12.40	10.20	22.60	36.80	4.28	40.40
27	21.60	16.52	5.08	10.80	8.90	19.70	35.58	0.00	42.82

TABLE 9.—*Composition of the water-soluble matter of alkali-treated cocoas.*

No.	Ash.			Alkalinity of ash (N/10 acid per gram of sample).			Protein.		Ash-free and protein-free solids.
	Total.	Water-soluble.	Water-insoluble.	Water-soluble.	Water-insoluble.	Total.	Total.	Precipitated by 1 per cent sulphuric acid.	
	P. cent.	*P. cent.*	*P. cent.*	*Cc.*	*Cc.*	*Cc.*	*P. cent.*	*P. cent.*	*P. cent.*
4	30.51	25.47	5.04	21.30	8.90	30.20	45.90	18.20	23.59
2	23.58	16.19	7.39	15.05	11.45	26.50	41.73	10.98	35.69
5	27.71	20.84	6.87	22.30	11.00	33.30	37.43	12.02	34.86
11	28.80	25.42	3.38	22.25	7.75	30.00	36.58	7.42	34.62
12	27.50	24.40	3.10	21.60	9.25	30.85	36.37	8.58	36.13
15	26.49	24.33	2.16	21.55	5.70	27.25	30.50	2.12	43.01
28	22.71	19.50	3.21	14.90	9.15	24.05	38.89	6.91	38.40
24	24.06	18.40	5.66	14.45	12.10	26.55	31.33	1.15	44.61
22	26.32	20.93	5.39	16.65	11.30	27.95	31.42	2.89	42.26
33	20.39	16.04	4.35	21.35	6.25	27.60	34.51	3.81	45.10
7	27.26	23.66	3.60	22.15	8.60	30.75	33.28	5.26	38.46
20	21.21	19.61	1.60	27.85	5.70	33.55	31.75	8.57	47.04
21	27.26	25.11	2.15	26.10	8.75	34.85	32.97	2.19	39.77
31	21.99	18.55	3.44	30.00	6.50	36.50	36.14	10.37	45.10
18	21.38	18.95	2.43	26.25	7.25	33.50	32.99	4.99	45.63
17	22.74	18.84	3.90	24.50	7.05	31.55	34.04	7.77	43.22
26	15.54	12.27	3.27	7.95	8.95	16.90	39.06	5.30	45.40
50	19.07	13.07	6.00	14.70	17.70	32.40	38.78	4.20	42.14
8	23.77	20.85	2.92	18.25	9.80	28.05	34.53	5.08	38.70
10	22.72	18.94	3.78	12.35	10.75	23.10	36.19	4.31	41.09
16	29.84	24.38	5.46	29.00	6.65	35.65	36.12	9.85	34.04
9	21.60	17.16	4.44	15.00	10.75	23.10	36.19	4.31	43.05
52	14.69	11.65	3.04	15.00	9.40	24.40	37.47	6.00	47.84
53	14.75	11.88	2.87	15.05	7.85	22.90	37.03	3.65	48.22
46	17.40	13.15	4.25	13.65	12.10	25.75	39.90	7.60	42.70
49	22.17	17.03	5.14	15.15	12.00	27.15	30.84	2.99	46.99
6	28.33	23.53	4.80	22.95	7.75	30.70	39.34	16.05	32.33
Maximum	30.51	25.47	7.39	30.00	17.70	36.50	45.90	18.20	48.22
Minimum	14.69	11.65	1.60	7.95	5.70	16.90	30.50	1.15	23.59
Average	23.32	19.26	4.06	19.53	9.27	28.80	35.95	6.74	40.64
34	17.43	16.36	1.07	19.20	3.40	22.60	34.47	8.82	48.10
35	26.88	23.51	3.37	23.00	6.35	29.35	31.66	6.53	41.46
37	19.82	18.05	1.77	17.05	5.80	22.85	37.77	11.50	42.41
38	20.23	19.11	1.12	21.55	4.85	26.40	38.98	8.66	40.79

As has been noted, the water-soluble matter of the alkali-treated cocoas has present a protein which is insoluble in 1 per cent sulphuric acid. This varies from 1.15 to 18.20 per cent of the solid matter. The greatest variation, however, is shown in the nonash, nonprotein matter, which varies from 39.87 to 57.96 per cent, with an average of 45.83 per cent, on the untreated cocoas, and from 23.59 to 48.22 per cent, with an average of 40.64 per cent, on the treated cocoas. Eleven samples of treated cocoas contain a smaller percentage of ash- and protein-free extract than the minimum of the untreated cocoa. This shows still more plainly what was shown in the analysis of the cocoas, namely, that the alkali treatment inhibits the solution of this nitrogen-free extract. On the other hand, the alkali treatment unquestionably increases, to a slight extent, the solubility of the protein.

ASH RATIOS IN UNTREATED AND TREATED COCOAS.

The ratio of the water-soluble ash to the water-insoluble ash was calculated on both the original cocoa and on the water-soluble matter; also, the ratio of the alkalinities of the soluble and insoluble ash was calculated on each of these. These results are listed in Tables 10 and 11.

TABLE 10.—*Ash ratios on untreated cocoas.*

No.	Water-soluble ash / Water-insoluble ash		Alkalinity water-soluble ash / Alkalinity water-insoluble ash		No.	Water-soluble ash / Water-insoluble ash		Alkalinity water-soluble ash / Alkalinity water-insoluble ash	
	Cocoa.	Water-soluble matter.	Cocoa.	Water-soluble matter.		Cocoa.	Water-soluble matter.	Cocoa.	Water-soluble matter.
19	0.55	1.26	0.61	0.63	55	0.45	2.28	0.48	0.72
23	.70	1.06	.49	.61	56	.49	1.43	.48	.75
25	.56	1.25	.47	.52	57	.38	1.88	.39	.75
32	.71	2.31	.52	1.04	58	.39	1.19	.46	.59
36	.65	1.81	.44	.36					
39	.60	.95	.46	.44	Maximum	.71	2.31	.61	1.04
40	.49	.55	.42	.48	Minimum	.28	.55	.34	.36
41	.51	.93	.34	.51	Average	.51	1.24	.41	.59
42	.28	1.03	.48	.53					
43	.62	.87	.44	.49	1	1.09	1.82	.65	.53
44	.62	1.24	.41	.51	13	1.33	3.46	.93	1.66
45	.45	1.02	.44	.49	29	1.11	1.46	.73	.93
47	.38	1.08	.39	.60	30	1.23	2.23	.77	1.54
48	.50	.80	.43	.50	3	3.16	4.70	1.38	2.43
51	.45	.68	.39	.46	14	1.26	2.45	.74	1.22
54	.39	1.18	.36	.67	27	.24	3.25	.19	1.21

Except on those samples which were treated with magnesium or ammonium carbonate, the soluble ash is invariably greater than the insoluble ash on the treated cocoas, the lowest figure (with the exceptions noted) being 0.81 and the average figure 1.88. With the exception of samples 1, 13, 29, and 30, which have been excluded from the general averages throughout on the ground of having been contaminated with more or less alkali-treated cocoa, the correspond-

ing ratio for the untreated cocoa has a maximum of 0.71, with an average of 0.51. This simply bears out the general belief that in a treated cocoa the soluble ash is approximately two-thirds of the total, while in an untreated cocoa it is one-third of the total.

TABLE 11.—*Ash ratios on alkali-treated cocoas.*

No.	Water-soluble ash / Water-insoluble ash		Alkalinity water-soluble ash / Alkalinity water-insoluble ash		No.	Water-soluble ash / Water-insoluble ash		Alkalinity water-soluble ash / Alkalinity water-insoluble ash	
	Cocoa.	Water-soluble matter.	Cocoa.	Water-soluble matter.		Cocoa.	Water-soluble matter.	Cocoa.	Water-soluble matter.
4	1.32	5.06	1.88	2.36	8	2.75	7.08	1.16	1.85
2	1.41	2.19	.82	1.32	10	2.03	5.00	.76	1.14
5	1.70	3.01	1.32	2.00	16	4.14	4.46	2.15	4.33
11	3.18	7.55	1.18	2.43	9	1.33	3.84	.79	1.40
12	2.72	7.83	1.35	2.33	52	1.20	3.83	.79	1.59
15	4.03	11.45	1.63	3.80	53	1.34	4.14	.69	1.91
28	2.57	6.08	1.07	1.62	46	.81	3.09	.63	1.13
24	1.36	3.25	.89	1.19	49	1.20	3.31	.90	1.27
22	1.68	3.88	1.01	1.47	6	2.70	4.90	1.62	2.88
33	2.95	3.68	1.31	3.41					
7	3.16	6.59	1.12	2.59	Maximum	4.14	12.20	2.19	4.87
20	2.49	12.20	2.12	4.87	Minimum	.37	2.18	.38	.83
21	2.88	11.60	2.19	3.00	Average	1.88	4.51	1.26	2.31
31	2.80	5.39	1.58	4.62					
18	1.59	8.78	1.44	3.63	34	3.67	15.36	1.37	5.61
17	3.20	4.83	1.60	2.47	35	2.98	6.96	2.93	3.62
26	.60	3.75	.45	.89	37	2.63	10.17	2.02	2.94
50	.37	2.18	.38	.83	38	4.58	17.16	3.00	4.44

Similar figures for the ash of the water-soluble matter show a wider variation, the ratio for the alkali-treated cocoa showing a minimum of 2.18 with an average of 4.51, while the ratio on the untreated cocoa has a maximum of 2.31, with an average of 1.24. Only one sample of the untreated cocoa is higher than the minimum of the treated cocoas.

The ratio between the alkalinity of the water-soluble ash and the alkalinity of the water-insoluble ash on the untreated cocoa varies from 0.34 to 0.61, with an average of 0.41. Only two samples have a ratio above 0.50. On the alkali-treated cocoas, however, the range is from 0.38 to 2.19, with an average of 1.26. Aside from sample 50, only one ran below 0.63. This sample had been treated with magnesium carbonate, which, of course, increased the alkalinity of the insoluble ash. In the same ratio of the water-soluble matter the untreated cocoas varied from 0.36 to 1.04, with an average of 0.59. Only one sample exceeded 0.75. The treated cocoas, on the other hand, varied from 0.83 to 4.87, with an average of 2.31, only three samples being less than 1.14. The ratios of the water-soluble and water-insoluble ash of the water-soluble matter and the ratios of the alkalinities of the water-soluble ash and the water-insoluble ash, on both the cocoa and the water-soluble matter, are fully as complete evidence of the use

of alkali treatment as is the commonly accepted ratio of the water-soluble to water-insoluble ash on the cocoa; in fact, in samples such as 26, which was treated with ammonium carbonate, and 50, which was treated with magnesium carbonate, the ratio of the water-soluble ash to the water-insoluble ash of the water-soluble matter and also the alkalinity ratio show the presence of an added alkali where the ordinary ratio does not.

ACTION OF VARIOUS ALKALIES ON COCOAS.

In Tables 3, 6, and 9, the alkali-treated cocoas are listed according to the alkali used and according to the percentage of that alkali, making it possible to note the action of the various alkalies in their various proportions. Results are not exactly comparable, because the same blend of beans was not used in each case, but, as showing the general effect of each of these alkalies, and as comparing the effects of the various alkalies, they are of great value. Samples 34, 35, 37, and 38 are, as has been mentioned, imported cocoas, and the alkali used is unknown. Also, as has been pointed out, sample 2, which was supposed to have been made with 2.5 per cent potassium carbonate, contains less than this amount, judging from the analysis, probably as little as 1 per cent. The only points worthy of note in this connection in Table 3 are: That the presence of sodium carbonate can be detected by the high alkalinities in practically every case; that ammonium carbonate exercises no effect on the normal cocoa ash, but that it is extremely difficult to remove all of the ammonia, as is shown by the fact that the indicated total protein on this sample is somewhat higher than normal; that the use of magnesium carbonate has the effect of increasing the water-insoluble ash and the alkalinity of the water-insoluble ash. In Table 6 the differences in the action of the alkali are more apparent. It will be noted that the treatment with 2.5 per cent potassium carbonate and 10 per cent of water gave the maximum total soluble matter, the use of the water evidently increasing the solubility of the cocoa. A curious point in this connection is the fact that as the percentage of potassium carbonate used increases, the soluble matter decreases, with the exception of the one mentioned where water was also used. Therefore, if the intention is to obtain a more soluble cocoa, the use of 1 per cent potassium carbonate rather than larger amounts is to be recommended. This difference is still more apparent when the soluble matter minus the ash is calculated. Sodium carbonate has a much greater solvent action than has the potassium carbonate. Slightly less protein is dissolved by sodium carbonate than by potassium carbonate, but the total soluble matter, ash-free soluble matter, and ash- and protein-free soluble matter are greater in those cocoas which have been treated with sodium carbonate. A mixture of the two, as shown in sample

16, combines to some extent the action of each, inasmuch as the total soluble matter is high and the soluble protein is high. The ash- and protein-free solids are, however, rather low, as compared with those in which sodium carbonate alone was used, thus seeming to indicate that potassium carbonate has an inhibitory action on the solution of these solids. Sample 50, in which magnesium carbonate was used, shows the lowest total water-soluble matter. This is partly due to the fact that no soluble alkali is added, as the ash-free solid matter is nearer to the average of the cocoas.

There seems to be no definite relation between the amounts of water-soluble protein insoluble in 1 per cent sulphuric acid and the alkali used. This figure varies somewhat with the percentage of alkali, although by no means in proportion. The color value of the solution also shows a very wide range, and seemingly follows no definite rule, except that the use of sodium carbonate gives the highest values.

It is interesting to note that three of the four imported cocoas show a total soluble matter and an ash-free soluble matter greater than the maximum of the domestic treated cocoa, and two of them show a greater ash- and protein-free soluble matter; also three show a higher percentage of soluble protein than the maximum of the domestic products, and all four show a higher color value than the maximum. With one exception, the total ash of these products is not appreciably greater than that of the domestic products, and the ash of the water-soluble matter falls well within the limits of the domestic products. This indicates that the increase in the other constituents is not the result of the addition of a larger amount of an alkali, such as sodium carbonate, but that the difference lies largely in the treatment which the cocoa undergoes.

APPEARANCE OF THE COCOAS.

The color of the dry cocoa in the samples examined varied widely, from a light brown to a deep reddish purple. Some of the untreated cocoas had a color nearly as pronounced as those that were treated. This color is not necessarily the result of any blend of beans, but depends largely on the treatment, especially the degree and rapidity of heating and cooling which the cocoa undergoes in its manufacture. The color of the dry cocoa seems to have but little connection with the color of the water solution. For instance, sample 27, a cocoa treated by a fermentation process, is among the darkest in the dry state, but the water solution of this is of a very light straw color, as may be noted by the fact that the color value of a 4 per cent solution in a $\frac{1}{4}$-inch cell was only 8.8. This is the most striking example of the fact that the color of the dry cocoa and that of the water solution bear little or no relation to each other. The same thing was noted,

to a lesser degree, in a great number of the other cocoas. In some cases a cocoa which seems to be of a quite light color when dry shows a very high color in the water solution. The color developed in the cocoa depends, of course, somewhat on the blend of beans used, but to a greater extent on the treatment which the product undergoes.

CONCLUSIONS.

The greatest effect of the alkali treatment of cocoas is apparently the increase in the color of the water solution. The total water-soluble matter is increased but slightly, and this increase is more than accounted for on the ground of the addition of the soluble alkali, the ash-free soluble matter being less in the case of an alkali-treated cocoa than in the case of the untreated cocoas. There is a slight increase in the amount of water-soluble protein by the alkali treatment. This, however, is more than made up for by the fact that the alkali treatment exercises an inhibitory action on the solution of the non-nitrogenous substances which are normally soluble in water. A portion of the water-soluble protein of the alkali-treated cocoas seems to be different from that dissolved in the untreated cocoas, inasmuch as it is rendered insoluble when the water solution is made 1 per cent acid with sulphuric acid. This is a point of difference between alkali-treated and untreated cocoas which might well serve for the detection of the alkali treatment.

As has been pointed out by other investigators, the alkali treatment increases the ratio of the soluble ash to the insoluble ash. This is true with all the alkalies employed, except ammonium carbonate and magnesium carbonate. Both of these, however, increase this ratio in the ash of the water-soluble matter, and this determination might serve as a clue to their presence. The ratio of the alkalinities of the ashes is still more pronounced than the ratio of the ash. The presence of an alkali-treated cocoa may therefore be proved by the high color value of the water solution, by the presence of a water-soluble protein precipitable in 1 per cent sulphuric acid, and by the increase in the ash ratios and the alkalinity ratios.

This investigation proves that the claim that the alkali treatment increases the amount of cocoa soluble in water is absolutely without foundation.

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